Aromatic Reactivity. Part XLIX.[1] Detritiation of [^{3}H]Phenanthrenes and 9,10-Dihydro[2-^{3}H]phenanthrene

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Rates of detritiation in trifluoroacetic acid at 70·0 °C have been determined for 1-, 2-, 3-, 4-, and 9-tritiophenanthrene and 2-tritio-9,10-dihydrophenanthrene. The rates relative to that for tritiobenzene are 900, 173, 385, 810, 1610, and 2740 respectively.

We have published a preliminary communication on the rates of detritiation of the several [^{3}H]phenanthrenes and of 9,10-dihydro[2-^{3}H]phenanthrene in trifluoroacetic acid at 70°.[2] The appearance of papers by Streitwieser and his co-workers,[3,4] in which our results are used, prompts us to describe the experiments on which they were based.

RESULTS AND DISCUSSION

The observed first-order rate constants at 70° for these reactions, are shown in the Table, along with the values of the rates relative to that for [^{3}H]benzene.[5] For the various positions of phenanthrene, the order of decreasing reactivity is 9 > 1 > 4 > 3 > 2, which compares with an order of 9 > 1 > 3 > 2 > 4 for nitration in acetic anhydride.[6] When log f is plotted against log f_N, where f_N is the rate factor for the same position in nitration,[6,7] the points for the 2- and 4-positions of biphenyl,[8] and all the positions of naphthalene,[9] fluorene,[10] and phenanthrene lie well about a straight line through the origin (*cf.* ref. 3), but the point for the 4-position of phenanthrene deviates badly from the line in a direction consistent with abnormally low reactivity in nitration; this can be attributed to steric hindrance in the nitration.

Rates of detritiation in trifluoroacetic acid at 70·0°

Compound	10^7k (s^{-1})	f [a]
[1-^{3}H]Phenanthrene	85·5	900
[2-^{3}H]Phenanthrene	16·4	173
[3-^{3}H]Phenanthrene	36·5	385
[4-^{3}H]Phenanthrene	76·8	810
[9-^{3}H]Phenanthrene	153 [b]	1610
9,10-Dihydro[2-^{3}H]phenanthrene	260	2740

[a] Rate relative to that for [^{3}H]benzene. [b] Measured by R. Baker.

Streitwieser and his colleagues have shown that our detritiation results for phenanthrene and some other polynuclear hydrocarbons are in good agreement with various theoretical indices of reactivity.[4] We add only that values of log f for the various positions of phenanthrene, naphthalene, biphenyl, and fluorene also correlate well with Brown's Z-values.[11]

The rate factor, f, of 2740 for the 2-position of 9,10-dihydrophenanthrene is, as expected, intermediate between those, *viz.* 163 and 16,800, for the corresponding

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4- and 2-positions of biphenyl and fluorene, respectively.[8,10] If the 2-position of phenanthrene behaved as a 1-position of a benzene nucleus bearing a 3-Me and 4-Ph group, a value of roughly 1000 would be expected for *f*, since 4-Ph and 3-Me substituents activate 163 and 6·1 times, respectively.[8,10] That the observed reactivity is some 2—3 times greater than this can be reasonably attributed to the fact that the two benzene rings are more nearly coplanar in 9,10-dihydrophenanthrene than in biphenyl, so that there is enhanced conjugation between the rings (see ref. 12).

It is noteworthy that when 9,10-dihydro[2-^{3}H]phenanthrene was made by treating with tritiated water the Grignard reagent made from 2-bromo-9,10-dihydrophenanthrene by the entrainment method, *ca.* 18% of the activity introduced was in the 9-position, indicating that some metallation had taken place there. An analogous result was noted in the preparation of [2-^{3}H]fluorene.[13]

EXPERIMENTAL

Preparation of Tritiated Phenanthrenes.—(i) 1-Aminophenanthrene,[14] m.p. 143—144°, was converted into 1-bromophenanthrene,[15] m.p. 106·5°. This (456 mg, 1·77 mmol) was converted into the Grignard reagent by entrainment with 1,2-dibromoethane in refluxing ether (150 ml); the reaction mixture was diluted with anhydrous benzene (50 ml). Tritiated water (0·5 ml) was then added cautiously, followed by a large excess of dilute hydrochloric acid. The organic layer was separated, washed, dried (Na_2SO_4), and evaporated to leave a solid; this was chromatographed in light petroleum (b.p. 60—80°) on alumina to give [1-^{3}H]phenanthrene (157·5 mg, 50%). The sample used for rate studies was recrystallized twice from ethanol and then sublimed *in vacuo*; it had m.p. of 99·5—100°.

(ii) 2-Aminophenanthrene [14] was converted into 2-bromophenanthrene,[15] m.p. 94—95·5°. A mixture of this (0·50 g, 1·95 mmol) with n-butyl-lithium (3·0 mmol) in ether under nitrogen was heated under reflux for 30 min. Tritiated water (0·5 ml) was added, and the mixture was worked-up as above but with distillation (b.p. 182—186°/12 mm.) in place of chromatography, to give [2-^{3}H]phenanthrene. The sample used for rate measurements, purified as under (i), had m.p. 99—100°.

(iii) [3-^{3}H]Phenanthrene, m.p. 99—100°, was obtained in similar fashion from 3-bromophenanthrene, m.p. 83·5—84°,[15] itself prepared from 3-aminophenanthrene.[16] The sample purified for rate studies as under (i) had m.p. 99·5—100°.

(iv) [4-^{3}H]Fluorene [10] (258 mg, 1·56 mmol) was metallated under nitrogen with n-butyl-lithium (1·56 mmol) in ether (100 ml). Treatment with formaldehyde followed by work-up gave [4-^{3}H]fluoren-9-ylmethanol which was chromatographed in light petroleum on an alumina column with benzene–ethyl acetate as eluant; it crystallized from light petroleum to yield material (176 mg, 57%) of m.p. 100—100·5° (lit.,[17] 99·5—100·0°). The product (131 mg, 0·67 mmol) in refluxing xylene was treated with phosphorus pentoxide (*ca.* 0·15 g) in small portions at intervals of 5 min for 30 min.[17] Ether was added to the mixture followed by water; the ethereal layer was then separated, washed, dried, and evaporated, and the residue was chromatographed on alumina with light petroleum as eluant; the product crystallized from methanol to give [4-^{3}H]phenanthrene (111 mg, 93%), m.p. 99—100°. The sample used for rate studies, purified as under (i), had m.p. 100°.

(v) [Preparation by R. Baker]. The Grignard reagent from 9-bromophenanthrene was treated with tritiated water; work-up and distillation gave [9-^{3}H]phenanthrene, m.p. 101°. The sample purified for rate studies as under (i) had m.p. 101°.

9,10-Dihydro[2-^{3}H]*phenanthrene.*— 2-Nitro-9,10-dihydrophenanthrene, m.p. 80—81° (lit.,[18] 81—82°) was reduced with hydrogen in presence of Adams catalyst (platinum oxide) in ethanol.[18] The solution was filtered, and the solvent was removed. The residue was dissolved in ether and the solution was shaken with hydrochloric acid. The amine hydrochloride (78%) was shaken with aqueous ammonia, and the product was extracted with ether. The extract was washed and dried (Na_2SO_4) and the ether was removed to leave 2-amino-9,10-dihydrophenanthrene as an oil. This was converted [14] into 2-bromo-9,10-dihydrophenanthrene (44%), m.p. 33·7—34·2° (Found: C, 65·1; H, 4·1; Br, 31·1. $C_{14}H_{11}Br$ requires C, 64·9; H, 4·3; Br, 30·9%).

The Grignard reagent was prepared by entrainment, as described under (i) above, and treatment with tritiated water followed by work-up left a solid; this was chromatographed in light petroleum on alumina and sublimed at 1 mmHg to give 9,10-dihydro[2-^{3}H]phenanthrene, m.p. 34—35° (lit.,[19] 34·5—35°), apparently contaminated with the [9-^{3}H]isomer, as indicated below.

Exploratory hydrogen-exchange studies on a sample of the product showed that *ca.* 18% of the tritium remained after 10 half-lives of the exchange, and it seemed that some tritium had entered the 9-position. Thus the bulk of the 9,10-dihydro[2-^{3}H]phenanthrene was refluxed for 18 h with 20% ethanolic sodium hydroxide, which removed 13% of the activity. Following this treatment, only 3·5% of the tritium remained after 10 half-lives of the exchange; allowance was made for this in the derivation of the rate constant.

Rate Measurements.—The purification of the acid and the details of the rate measurements have been described previously.[5,20] The rate constant for [*p*-^{3}H]toluene in this medium agreed excellently with that previously recorded.[21] Good first-order plots were obtained in all cases.

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